THE DEPOSITION OF ZINC ON STEEL

BY

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ARMOUR INSTITUTE OF TECHNOLOGY

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THE DEPOSITION OF ZINC ON STEEL

A THESIS

PRESENTED BY

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TO THE

PRESIDENT AND FACULTY

OF

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PREFACE.

The purpose of this work is to study conditions under which a bright, uniform, adherent coating of zinc may be deposited on steel electrolytically. The following would be the advantages of such a method over the hot- galvanizing methods:

1.) From a suitable electrolyte a prefectly adherent and coherent coating could be deposited and the thickness of the coating can be controlled, whereas only a fairly thick deposit can be obtained from hot-galvanizing.

2.) The physical qualities of the deposited metal is much more completely under the control of the operator.

3.) The amount of zinc per unit area of surface has greater protective action against certain tests.

4.) Tempered steels may be plated safely electrolytically, whereas ordinary hot methods are liable to be detrimental to the physical properties of such steels.

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5.) A smoother and brighter deposit may be obtained.

6.) There is less loss of metal in dross and waste.

7.) The non-crystaline deposit, and the greater purity of the deposited metal, means less disintegrating action toward weak acids and alkalies or even water.

It is desirable to divide the work into two parts, which are as follows:

Part one: The survey of the various methods employed to-day in obtaining a protective coating of zinc on steel, and various electrolytes which have been tried for the electrodeposition.

Part two: The theory of the deposition and a survey of the work done in the laboratory.

I am here taking the opportunity to acknowledge my indebtedness to my instructors, Prof. Harry Mc Cormack, and Prof. C. A. Tibbals, whose interest and initiative help has made possible such accomplishments as are herewith noted. W.W.K.

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Part One.

The survey of the various methods employed to-day in obtaining a protective coating of zinc on steel and various electrolytes which have been tried for electro-deposition.

The Deposition of Zinc on Steel.

Introduction.

The methods employed to-day for the deposition of zinc on steel may be divided into three general classes, which are, first, the old and popular method known as hot-galvanizing, where the article is immersed in molten bath of zinc, second, the sherardizing which is the treatment of the article with zinc dust under pressure and heated to an elevated temperature, and, third, the electro-deposition of zinc.

There is only one company which deposites zinc on steel commercially from an electrolyte and obtains a coating which is adherent, uniform in thickness and lustrous when removed from the bath. However there are many electrolytes which yield an adherent deposit, but which is dull.

The Deposition of Zinc on Steel.

Part One.

Hot-Galvanizing.

For a long period, iron and steel has been given a protective coating of zinc by means of hot-galvanizing. This method consists essentially of first cleaning the article in a pickling solution as 1 to 16 sulphuric acid solution, hot soap or sodium hydroxide solutions (concentrated), or other similar solutions. After the article is thoroughly cleaned, it is immersed in a molten solution of zinc which is above 419°C., the melting point of zinc, and less than 918° C., which is the boiling point. A thin coating of zinc adheres to the surface of the metal and is very crystaline in its structure.

This method gives a fairly uniform coating but the coating is of only one thickness and can not be made heavier or lighter. There is always a certain amount of zinc lost in the dross formation.

The Deposition of Zinc on Steel.

Sherardizing.

The sherardizing is a new method which fuses the zinc with the surface layer of the iron, and has been thoroughly worked out by the Couper-Coles Company. The method which is employed with flat articles such as plates, etc., consists essentially of packing the article with zinc dust in a chamber and heating it, under pressure, to an elevated temperature. The steel will then not only be coated with zinc but the outer layer of the article will fuse with the zinc to form an alloy. This is a very desirable coating, but can only be applied to flat surfaces, rods and tubes.

There has been considerable amount of experimental work done with respect to heating the articles in an atmosphere of zinc dust and with little modification the process will soon be a commercial success. The coating obtained by this method is superior to that of hot-galvanizing.

The Deposition of Zinc on Steel.

Electro-deposition.

The essentials of obtaining a desirable deposition from an electrolyte are, a correct electrolyte to start out with, the correct current density with the temperature of operation and a burnished surface at the start to obtain a bright coating.

The Simmons Company have developed a method by which it is possible to deposit a prefectly bright coating of zinc on wire fabric and other small articles. The electrolyte they use consists of zinc sulphate solution with certain addition reagents. The current density at the anode is from 25 to 50 times as great as that of the cathode. The reason given for this difference, is that super sulphuric acid and ozone are formed at the anode, thereby oxidizing any hydrogen which may be formed at the cathode, which is essential as the liberation of the hydrogen is liable to cause a rough deposit.

The Deposition of Zinc on Steel.

The process is continuous, as the long coil or spring passes from the pickling vats thru the washer or water vats, and then thru the electrolytic bath. The spring is made the cathode and moves thru the electrolyte at a speed so that when it comes to the other end of the bath it has the desired thickness of coating. This process is a commercial success and its detailed operations are kept secret.

The Couper-Coles patented electrolyte consists of:

$ZnSO_4 \cdot 7H_2O$, - - - - - - - - - - 40 oz. - 1.25 KG.
Ferrous sulphate, - - - - - - 5 oz. - 156 gr.
Water, - - - - - - - - - - - - - 1 imp.gal - 1 L.
1 1-5 U.S. gal.

In addition to these there is a small amount of glucose, glucosides, or licorice extracts added to the solution.

The ferrous sulphate gradually oxidizes to ferric sulphate by the action of the atmosphere and taking up acid from the bath, and so tends

to kept the electrolyte neutral. The anode consists of a lead plate or electrode; and the concentration of the electrolyte is kept constant by pumping the solution through scrubbers containing coke, and vessel containing zinc dust and zinc oxide, thereby bringing back the solution to the corrent concentration and reducing the ferric salts to the ferrous state. No statement is made with respect to the luster of the finished product, but only that an adherent uniform deposit is obtained.

If powdery precipitates are obtained, it is said to be due to the formation of the oxide or hydroxide of zinc.

A series of experiments has been made by Philips with the addition of the sulphates of sodium, potassium, ammonium, aluminum, and magnesium to zinc sulphate. The results obtained using these electrolytes, at the correct current density, are adherent deposites, but,

which are dull bluish gray color. The temperature at which the operation was carried out was from 50° to 70° C. When magnesium sulphate was added, it was added in molecular proportions with the zinc sulphate so as to form a double sulphate salt. The quantities used are: zinc sulphate 30 oz., magnesium sulphate 25 oz., and water 1 imp. gallon, which is equivalent to $1\frac{1}{5}$ U.S. gallon. Similar results are obtained with the sulphates of sodium and potassium. The proportion of the aluminum sulphate and zinc sulphate is $1\frac{1}{2}$ oz. and 2 pounds respectively to 1 imp. gal., or 1 1-5 U.S. gal. of water. The aluminum sulphate may be substituted by 4 oz. of alum. Higher densities make it possible to operate with greater current densities. The aluminum sulphate dissociates into aluminum hydroxide and sulphuric acid in the presence of the water, former acting as a colloid. It is said that colloids prevent the formation of crystals or at least reduce the size of them. Therefore a greater cur-

rent density may be used.

The last two solutions give a bluish gray deposit which may be readily burnished. The coating is adherent and has a uniform thickness.

The solution tried by Richter consists of zinc sulphate 50 oz., and water 1 1-5 U.S. gallon. The solution is very rich in metal and the current density is from 25 to 30 amperes per sq. ft. The anodes may be either wrought iron, cast iron, or steel, and the area must be greater ~~than~~ at the anode than at the cathode. The temperature of the electrolyte should be about 50°C., or more, and never less than 30°C. The deposit from this solution is very apt to be granular.

The forementioned solutions are either neutral or slightly acid. There are however a few distinctly alkaline solution which may yield a satisfactorly deposit, but the expense is too great for commercial value. The typ-

ical one is Watt's cyanide solution, patented in 1855, and uses 200 oz. of KCN, dissolved in 20 gal., of water, and 80 oZ. of zinc added which is dissolved by the addition of ammonium liquor. The solution is then stirred and filtered before using. The anode is made of zinc while the cathode is preferrabily copper.

Another alkaline solution used, consists of zinc sulphate, potassium cyanide, and ammonium carbonate, dissolved in water.

Dr. Kern states that zinc may be deposited from a solution of zinc fluosilicate 12 parts; aluminum sulphate, 10 parts; ammonium sulphate, 5 parts; and water, 100 parts.

A through investigation has been made by Snowdon in respect to the deposition of zinc from various concentrations of zinc sulphate solutions with and without the addition of resorcinol in both sulphuric acid and sodium hydroxide solutions. The temperature for the

various series of runs were 20°, 40°, and 70°, with the variation of current density from .5 to 7.0 amperes per sq. dm. The various solutions may be tabulated as follows:

A.) N-2 Zn SO_4 plus N-50 H_2SO_4,
B.) N-2 " " " N-5 " ,
C.) N-2 " " " N-50 " plus N-10 resorcinol.
D.) N-10 " " " N-50 " ,
E.) N-10 " " " N-5 " ,
F.) N-10 " " " N-50 " plus N-10 resorcinol.
G.) A saturated solution of $Zn(OH)_2$ in 3N NaOH.
H.) Addition of 60 gr. of solid NaOH to 2 L. of solution G.
I.) Addition of 11 gr. resorcinol N-10 per L., of solution G.
K.) Dilute the solution of G., to ¼ with 3N NaOH.
L.) Addition of 60 gr. solid NaOH to 2 L. of solution K.
M.) Addition of 11 gr. resorcinol to 2 L. of

solution K.

The summary of the results and conclusion is that the deposit is not as satisfactorly from alkaline solutions as from acid or neutral solutions. An increase of temperature within a limited extent and an increase in concentration causes an increase in size of the crystals. Certain reagents as formaldehyde will decease the size of the crystals. Snowdon also states that increase in current density will decrease the size of crystals, but this statement does not confirm that of other authorities. The addition of resorcinol should cause a darker deposit of zinc to from. None of the deposits are stated to be bright.

Other solutions which have been tried are zinc sulphate, zinc naphthalene di-sulphonic acid, with small quantities of aluminum sulphate, or zinc chloride. All of which yield dull deposits.

The Deposition of Zinc on Steel.

The General Electric Company deposit zinc from a molten solution of 100 parts of zinc chloride, 10 - 50 parts of zinc dust, and 3-10 parts of ammonium chloride. No other explanation of the method is given.

The various addition reagents which are only added in small quantities, are as follows: sugars, glucosides, yeast or other ferments, glue, licorice extracts, oxalic acid, citric acid, formaldehyde, and few of the essential oils.

Summary of Results.

With low current density, hydrogen is formed at the cathode, because zinc is high in the electro-motive series, therefore highly electropositive. Therefore high current density must be used, which means concentrated electrolytes must be used, not less than 4-5 oz. zinc per gallon, or 25-31 gr. zinc per liter.
The addition reagents reduces the size of the crystals and also increase the temperature at which the zinc may be deposited, to limited extent.

Part Two.

The theory of the deposition and a survey of the work done in the laboratory.

The Deposition of Zinc on Steel.

Introduction.

The work consists in developing a method, by which a lutrous deposit of zinc may be obtained, and, which will resist the action of corrosion.

In doing so, various electrolytes were used, and the resulting deposits were examined and subjected to various tests, usch as resistance to scratching, thickness of coating, resistance to concentrated copper sulphate solution, and a microsoopical examination of the surface.

A study was also made of the electrolyte with respect to the change in concentration, and acidity.

The Deposition of Zinc on Steel.

Part Two.

Theory.

The theory of corrosion:- When two different metals are placed into a solution, which is ionized, and the dry ends are connected by means of a conductor, a current flows thru the system. Now, if we have a piece of steel covered with a zinc deposit, which is not prefect, so that part of the iron is exposed, and then have the surface covered with water containing small amount of organic matter,or carbonic acid, or soluble salts, just enough to ionize the water, the cell is completed. The water is ionized into two ions of hydrogen, carrying each, one positive charge, and into one oxygen ion which carries two negative charges. The iron and zinc are of two different potentials, the latter being the greater, therefore in the cell the kation, which is the oxygen ion, will travel to the kathode, give up its charge and attack the zinc, which will go into solution. The anion which is the negative ion or hydrogen

ion will travel to the anode, give up its charge and escape at the cathode as nascent hydrogen. Therefore the zinc will go into solution while the iron remainds unattacked, and the current in the cell travel from the zinc to the anode or iron. As long as there is a trace of zinc left in contact with the electrolyte and steel or iron, the latter will not corrode. If the plate is covered with tin deposit, which is below iron in the electro-motive series, the current will flow in the cell from the iron to the tin and the iron would corrode leaving the shell of tin.

The theory of plating:- When a current is sent thru a solution of zinc sulphate, the zinc sulphate will dissociate into zinc ion, or kation carrying two positive charges; and sulphate (SO_4) ions called anions, carrying two negative charges. The kation will travel to the cathode, give up its charge and deposit on the cathode as metallic zinc, while the anion

will travel to the anode, give up its charge and become free SO_4 which can not exsist as such for any length of time. If the anode consists of zinc, the SO_4 will react to form zinc sulphate, and thereby theoretically kept the concentration constant. Of on the other hand the anode consists of an insoluble metal as platium or lead, the SO_4 will not attack these, but will attack the water to from sulphuric acid and liberate oxygen at the anode. Thus the concentration of the bath constantly deceases. The sulphuric acid is ionized into hydrogen ions and oxygen ions. The oxygen ion having two negative charges will travel to the anode, give up its charge, and will be liberated at the anode as gaseous oxygen. The hydrogen in the similar manner will be liberated at the cathode. as nascent hydrogen, which is undesirable in plating, because the gase bubbles will not leave the plate fast enough,and thereby give an uneven, rough surface.

The Deposition of Zinc on Steel.

The liberation of hydrogen at the cathode is not only detrimental to the finish of the deposit on the plate, but also means a loss in the current, therefore deceasing the efficiency of the cell.

In order to pass a current thru the cell, a certain potential or pressure is required to pass the current, and thie potential is called the decomposition voltage.

It was observed by Faraday that the amount of deposition in a cell which has an electrolyte of dilute sulphuric acid, and electrodes of platium, is proportional to the amount of electricity flowing thru the cell. We have here, then, a direct proportion between the quantity of matter and quantity of electricity. For example, each gram of hydrogen liberated by an electrical current corresponds to the passage through the electrolyte of 96,493 coulombs which is equivalent to one Faraday. It is independent of the strength of the current,

which liberates the hydrogen, upon the time of liberation, and the strength of the acid, so long as the hydrogen alone is liberated; the result is always the same,-a given amount of electricity, in each case liberates the same amount of hydrogen. What is here true of hydrogen is also true of the metals, and groups. By experiment it has been found that one Faraday will liberate one gram of hydrogen, (more accurately 1.0076 grams). The electrochemical equivalent is the amount of substance liberated by the same amount of current which will liberate 1.0076 grams of hydrogen. This relation is called the Faraday Law. The electro chemical equivalent is the same as the chemical equivalents.

This means that one Faraday is passes thru the zinc sulphate cell, theoretically 65.37 divided by 2 equals 32.65 grams of zinc will be ionized.

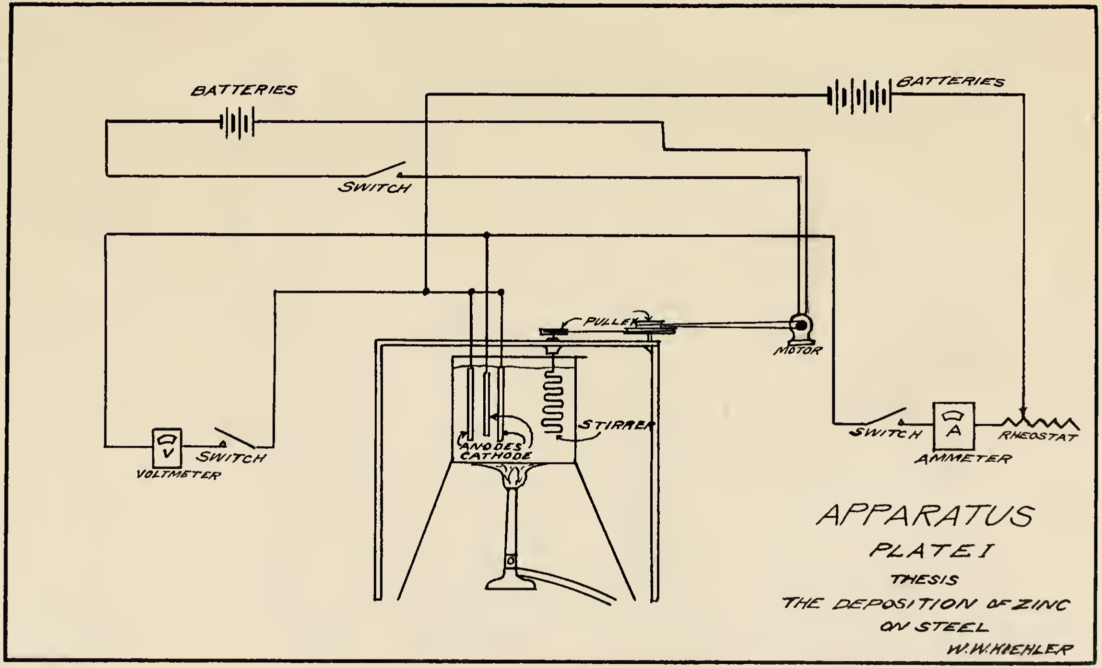
From the above theory, it can be seen

that the deposition of the zinc is independent of the voltage, as long as the voltage is great enough to pass a current thru the cell. Therefore it is profitable to operate at the lowest voltage possible which will give the desired deposit, in order to decrease the cost of the power, which is equal to the voltage times the amperage.

Apparatus.

The apparatus consisted of two sets of storage batteries, one voltmeter (0-10), one ammeter (0-25), a 1.5 liter beaker, two single pole single throw switchs, two zinc anode plates, several rolled steel plates (5cm. x 10cm.), stirring paddle, reduction pulley, small 6-volt motor registered as 1-8 horse power motor, insulated stands, clamps, bunsen burner, and flame protector.

The apparatus was connected as shown on the plate (Plate one). The ammeter, one switch steel plates, two anodes, and rheostat are con-



APPARATUS
PLATE I
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nected in series with each other. The two anode plates are connected in parallel with each other, and the anodes and cathode are connected by submerging them in the electrolyte. The voltmeter was connected across the anodes and cathode with a switch, in series.

The electrolyte was stirred by means of a stirrer which was rotated by means of a small motor. As the motor was too weak to drive the paddle direct, the pulley of the paddle was connected to a reducing pulley and then to the motor, which as connected to the other set of cells.

The solution was heated by means of a bunsen butner and the temperature was controlled within two to three degrees.

Operation.

The first step in the deposition is to throoughly clean the plates or article to be plated. The material to be plated was cold rolled steel

plates, which had a coating of oxide and a few rust spots. The plates were first cleaned by chemical means. A solution of 1 part of concentrated sulphuric acid, sp.gr. 1.84 to 16 parts of water, was made up; and the plates immersed for about 50 minutes. At the end of this time the coating of oxide was loosened, and the plates were removed and washed with water, dried and rubbed off with emery cloth until a clean, fairly smooth surface was obtained.

Another good pickling solution consists of 1000 parts of water, 1444 parts of concentrated sulphuric acid, and 60 parts of 48% HF. The solution is thoroughly agitated with a wooden paddle before using, and the article is placed in the solution, which is then heated on the steam bath for ten minutes.

After the plates are cleaned and burnished with emery and, having the electrolyte made up, the plates are dipped a few minutes in a strong hot sodium hydroxide solution to remove any trace

of grease which might adhere. It is then quickly washed with water and placed in the electrolyte, connection being made with the cathode clamp. The current is turned on, and the rheostat adjusted for the desired amperage. The amperage, voltage, initial and final time recorded. After the plate had the desired thickness of coating, the current was turned off, the plate removed, washed and dried. It was then subjected to various tests and examined.

Electrolytes.

The first electrolyte used consisted of 200 grams of zinc sulphate, 10 grams of aluminum sulphate, dissolved in water and made up to one liter. 10 c.c. of formaldehyde was added. This electrolyte has been tried and the reason for using it was to familarize myself with the nature of the method of plating. The first run was made at 11 amperes and yielded a loose deposit. The second at 5 amperes which gave a dull bluish gray, smooth adherent deposit.

The Deposition of Zinc on Steel.

Since the previous experimental work shows the tendency to get a substance in colloidal form in the electrolyte, I thought that by dissolving a small amount of cotton in a concentrated solution of zinc chloride, the zinc could be deposited. The electrolyte consisted of 400 grams of zinc chloride dissolved in water and made up to one liter. Then 200 milligrams of cotton were dissolved in the solution. Here the first difficulty was met. It was found that the cotton only dissolved upon heating for several hours.

A few runs were made using .1, .5, 1.0 and 1.5 amperes per sq. dm. The results obtained were not very satisfactory as after two plates were made, the cotton had all precipitated from the solution, and the next deposit came down granular and uneven. More cotton had to be dissolved before better results were obtained, but these were not as good as the first. This electrolyte was considered as useless and a failure.

The Deposition of Zinc on Steel.

From a strong solution of zinc sulphate the deposit will be crystaline if the current density is too great; and uneven due to the liberation of hydrogen if the current density is too small. If the hydrogen could be oxidized rapidly enough, the deposit should come down smooth. This was tried by dissolving 400 grams of zinc sulphate in a liter of water and adding a small amount of potassium permanganate solution. Similar runs were made as in the zinc chloride solution, and the results obtained were not satisfactory. The MnO_2 was preipitated and adhered to the plate, causing irregularities in the surface. The electrolyte was discarded as a failure.

The next electrolyte which was tried consisted of a N-2 solution of zinc sulphate with the addition of 20 grams of chrome alum. per liter, and a small amount of gum tragacanth. The solution was boiled to remove the gases or air from the solution, and then filtered thru a towel so as to remove any gum tragacanth which

had not dissolved. The solution was cooled to 85°C., and a series of runs were made using a current density of 1, 3, 5, and 7 amperes per sq. dm. The results obtained were more satisfactory than any of the other previous ones. The deposits, which were fairly good, were dull smooth, adherent, but with a some what of an crystaline appearance.

The solution was then cooled to 70° and the following series of run made:

1) 1 amp.per sq.dm., .3 v., good adherent deposit.
2) 3 " " " " , .6 v., very good deposit.
3) 5 " " " " , 1.1 ", not as bright as 2.
4) 7 " " " " , 1.7 ", becoming crystaline.
5) .5 " " " " , .15 ", H_2 formed at cathode.

All of these runs were ten minute duration, except the last which was 25 minutes.

After the solution was cooled to 45°C., a similar set of runs were made. The following are the amperages and voltages used for each run respectively:

The Deposition of Zinc on Steel.

1) .5 volts - 1 amp. per sq. dm., 2) .9 volts - 3 amp., 3) 1.3 volt - 5 amp., 4) 2.4 volts - 10 amp., and 5) 3.5 volts - 14 amp. The deposites were not as good as those at 70°C., and the third and fourth ones had granular edges while the fifth grew "trees".

A series of runs were made at a temperature of 25° and in all cases the deposits were uneven dull and not adherent.

At room temperature the deposits came down spotted or discolored.

The next electrolyte consisted of a N-4 solution of zinc sulphate with the same amount of chrome alum and small amount of gum tragacanth. The solution is boiled and filtered before using. A similar set of runs were made at the same temperatures and amperages respectively as before. The results obtained shoed the same characteristics as regards to the temperature, and current density, but in no case was the deposit as bright.

The Deposition of Zinc on Steel.

When ten grams of zinc chloride was added to the previous electrolyte, no change in the results were obtained.

Several plates were burnished and plated with the N-2 zinc sulphate solution and its addition reagents, at 70°C., using a current density of 1.0 and 2.0 amperes respectively. The deposits came down fairly bright and the latter being the best. These plates were subjected to scratching test and microscopic examinations.

Two plates were coated at 1 ampere per sq. dm., and the deposit of the zinc dissolved, and the solution tested for zinc content. Two other plates were plated at 2 amp. sq. dm., and their deposit dissolved and analyzed.

Tests.

The first test to which the deposit was subjected to was the scratching test, or its resistance toward scratching. This was done

by taking the sharp point of a file and scratching the surface of the deposit. If the deposit was adherent, the file would only scratch which was bright; but if the deposit was not adherent the file would loosen the film of deposit quickly from the surface of the steel and form bubbles which on farther scratching would fracture the film and the deposit could be peeled off.

The test for corrosion was made by dipping the zinc coated plate into a saturated solution of copper sulphate for a period of one minute, and then taking it out and rinsing the plate under a tap, shaking rapidly. While the plate is in the copper sulphate solution, the copper in the solution will replace the zinc and the latter will deposit loosely on the surface as a black percipitate. This zinc will go in solution as zinc sulphate. If there is any spot of steel which is not covered with zinc the copper will replace the iron and the deposit of copper film over this spot which will not

be washed away by the water. If this is repeated using fresh copper sulphate solution a comparative test could be made between the various deposits. The reason for the copper replacing the other two metals, is because they are higher in the electro-motive series and therefore will replace any metal in solution which is lower in the electro-motive series.

The burnished plates were used for microscopic examination. When the plate which had the zinc deposited at 1 amper per sq. dm., was put under the microscope, there were small gas bubbles within the deposit. These gas bubbles could not be seen with the unaided eye, but showed up clearly when magnified about 600 diameters. The bubbles were always in groups which were needle shape. The microscope showed no spots which were not coated, or pinholes in the deposit. When this plate was cleaned with fine emery cloth, most of the bubbles disappeared, and left no uncoated spots.

The Deposition of Zinc on Steel.

The plate which had the zinc deposited at 2 amperes per square decimeter, there were no bubbles of gas to be detected, and the deposit appeared smooth and regular with no breks or"pin-holes" in the deposit.

The thickness of the coating was next determined. This can also be calculated theoretically as follows:

First the plate which had the zinc deposited at 2 amp. per sq. dm. The pate used hada total area of 100 cm^2 or one decimeter, squared. The time of deposition was five minutes, which equals 300 seconds.
The total number of coulombs is equal to the amperage multiplied by the time.

$$300 \times 2 = 600 \text{ coulombs.}$$

$$96{,}493 \text{ coulombs} = 1 \text{ Faraday.}$$

Now one Faraday will deposit or liberate 1.0076 grams of hydrogen, or since the electrochemical equivalent of zinc is two, will liberate $65.3 \div 2 = 32.65$ grams of zinc.

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Therefore the amount of zinc deposited by a current of 2 amperes for five minutes is equal to,

$$\frac{600}{96,493} \times 32.65 = .2032 \text{ grams of Zn.}$$

Now the density of zinc is 7 (average), hence dividing the weight by the density gives us the volume of zinc, which is as follows:

$$.2032 \div 7 = .0290 \text{ c.c.}$$

The total area of the plate is 100 sq.cm., therefore dividing the volume by the area, we will get the thickness of the deposit:

$$.0290 \div 100 = .000290 \text{ cm.}$$

$$.00290 \text{ mm. thick.}$$

For the plate which has the zinc deposited at 1 ampere, the zinc deposited is equal to one-half of that of the one above, or,

$$.2032 \div 2 = .1011 \text{ grams of zinc.}$$

The thickness of the deposit will be one half that of the one above which is equal to,

$$.0029 \div 2 = .0015 \text{ mm. thick.}$$

The Deposition of Zinc on Steel.

The actual thickness of the deposit is obtained by dissolving the deposit in 50 c.c. 1:1 dilute hydrochloric acid; and after the action ceases (the steel being acted upon very slowly) the plate was removed, washing it free from acid. The solution was then made alkaline with ammonium hydroxide, and then just acid to litmus with dilute HCl. Then 3 c.c. of concentrated HCl was added in excess. The solution was diluted to 200 - 250 c.c. and heated to a boiling. It was then titrated while hot with potassium ferrocyanide solution, using a 4% solution of Uranium nitrate as an external indicator.

Two plates having the zinc deposited at 2 ampere per sq.dm., used 19.50 c.c. and 19.95 c.c. respectively.

The plates plated at 1 ampere per sq. dm., used 8.60 and 8.92 c.c. respectively. The time of precipitation being for all plates five minutes.

The Deposition of Zinc on Steel.

The standardization of the potassium ferrocyanide. 90 grams of $K_4Fe(CN_6)_6$ were dissolved in two liters of distilled water. Then two samples of zinc oxide (ZnO), each .4978 grams, were dissolved in 20 c.c. concentrated hydrochloric acid, diluted somewhat, and ammonium hydroxide added drop by drop to alkalinity. Dilute hydrochloric acid is added until the solution is just acid to litmus, and 3 c.c. of concentrated HCl added in excess. The solution was diluted to 200-250 c.c. and heated to a boil. While hot, it is titrated with potassium ferrocyanide solution. A 4% Uranium nitrate solution was used as an external indicator.

Sample A used 42.35 c.c. $K_4Fe(CN_6)_6$

Sample B used 42.40 c.c. $K_4Fe(CN_6)_6$

.4978 grams of ZnO $\equiv$ .4000 grams of zinc.

42.35 c.c. $K_4Fe(CN_6)_6$ $\equiv$ .4000 grams of Zn.

1.00 c.c. " $\equiv$ .00943 grams of Zn.

42.40 c.c. " $\equiv$ .4000 grams of Zn.

1.0 c.c. " $\equiv$ .00945 grams of Zn.

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average 1.0 c.c. $K_4Fe(CN_6)_6 \equiv .00944$ gr. Zn.

Now the plates which used a current density of 2 amp. per sq.dm., used 19.5 c.c. and 19.95 c.c. of potassium ferrocyanide.

19.50 c.c. $K_4Fe(CN_6)_6 \equiv 19.50 \times .00944 = .1842$

19.92 c.c. " $\equiv 19.92 \times .00944 = .1883$ grams of zinc.

The density of the zinc being 7.0 average, the volume is,

$.1842 \div 7 = .0263$ c.c. of zinc.

$.1883 \div 7 = .0269$ c.c. of zinc.

The area of the plates were 100 sq. cm., therefore dividing the volume by the area, we get the thickness of the deposit, which is equal to, $.0263 \div 100 = .000263$ cm, $= .00263$ mm.

$.0269 \div 100 = .000269$ cm, $= .00269$ mm.

The plates operated at a current density of 1 amp. per. sq.dm., used 8.60 c.c. and 8.92 c.c. Then the amount deposited equals,

$8.60 \times .00944 = .0812$ grams of zinc.

$8.92 \times .00944 = .0842$ grams of zinc.

Then the volume of the zinc deposited is equal to,

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.0812 ÷ 7 = .0116 c.c. of zinc.

.0842 ÷ 7 = .0123 c.c. of zinc.

The thickness of the deposit is obtained by dividing by the area of the plate which is 100 sq. cm., then,

.0116 ÷ 100 = .000116 cm. = .00116 mm. thick.

.0123 ÷ 100 = .000123 cm. = .00123 mm. thick.

The efficiency of the method:- For the first two plates:-

Theoretically, .2032 grams deposited

Actually, av., .1863 grams deposited

$$\text{Efficiency} = \frac{.1863}{.2032} \times 100\% = 91.9\%$$

The efficiency of the second set of plates,

Theoretical amount of zinc, .1011 grams Zn.

Actual amount of zinc, av., .0827 grams of Zn.

$$\text{Efficiency} = \frac{.0827}{.1011} \times 100\% = 81.2\%$$

The low efficiency of the second set is due to the liberation of hydrogen and other side reactions.

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Some attention was given to the stability of the concentration in respect to the zinc content. Two five c.c. samples was taken before plating and after four depositions, two more samples were taken, each being five c.c.

The 5 c.c. sample was diluted somewhat and 40 c.c. of 1:1 dilute hydrochloric acid was added, then made alkaline with ammonium hydroxide and boiled. All of the chromium is precipitated and some of the zinc. The solution is filtered while still hot and the filtrate saved. The precipitate is dissolved in an Erlenmeyer flask with a minimum amount of HCl, and then a solution of sodium carbonate is added drop by drop until a permanent turbidity was produced. Then drop by drop of HCl is added until the precipitate dissappears. It is then treated with barium carbonate in a water susendion until an excess is added, which on shaking will remain at the bottom of the flask. The solution is then covered and set aside for a few hours,

shaking at intervals. The solution is filtered off by decantation, and the precipitate washed several times by decantation with water. The filtrate is added to the first solution and make alkaline with NH_4OH. Then drop by drop with dilute HCl, the solution is made just acid to litmus paper, then adding 3 c.c. concentrated HCl in excess. The solution is heated to boiling and titrated with potassium ferrocyanide while hot. The Barium carbonate precipitates the chromium and only a very small trace of Zn.

The sample taken before electrolysis used 21.50 c.c. and 21.85 c.c. respectively. Their zinc content equals,

21.50 c.c. x .00944 = .2029 gr. of zinc.

21.85 x .00944 = .2063 gr. of zinc.

The equivalent amount of $ZnSO_4 \cdot 7H_2O$, equals,

$$\frac{ZnSO_4 \cdot 7H_2O}{Zn} = \frac{287.3}{65.3} = \frac{x}{.2029} \quad x = .8928 \text{ grams}$$

$$= \frac{x}{.2063} \quad x = .9077$$

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The equivalent amount of zinc sulphate per liter, equals,

.8928 x 1000 ÷ 5 = 139.1 grams

.9077 x 1000 ÷ 5 = 141.5 grams

(before) average = 139.3 grams

After electrolysis, samples used 21.61 c.C, and 21.92 c.c. respectively. The zinc content equals,

21.61 x .00944 = 2040 grams of zinc.

21.92 x .00944 = 2069 grams of zinc.

The amount of $ZnSO_4 \cdot 7H_2O$ per liter equals,

$$.2040 \times \frac{287.3}{65.3} \times \frac{1000}{5} = 139.5 \text{ gr. per liter.}$$

$$.2069 \times \frac{287.3}{65.3} \times \frac{1000}{5} = 142.1 \text{ gr. per L.}$$

The average after electrolysis, 140.8 gr. per L.

From the above data there is a very little increase of zinc, which might be due to the formation of the sulphuric acid, which is electrolysised and on electrolysis yield zinc sulphate at the anode and hydrogen at the cathode.

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Summary.

The results may be summarized as follows:

A fairly bright deposit may be obtained from the electrolyte, containing 143.6 grams of zinc sulphate ($ZnSO_4.7H_2O$), 20 grams of chrome alum ($K_2SO_4.Cr_2(SO_4)_3.24H_2O$), and a small amount of gum tragacanth per liter of water. The current density being from 2 to 4 amperes per square decimeter, and the temperature between 70 and 75° C., It is understood that the article must be lustrous before starting. The anode must be greater than the cathode.

Zinc can not be deposited from a solution poor in zinc content, nor at a low current density. Higher current density causes crystaline deposit, and lower density causes liberation of H_2 at the cathode. To a certain limit, increase of temperature improves the deposite and decreases the voltage for the same current density.

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Appendix.

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Finish.